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Anionic Polymerization of Acrylic Monomers. 16. Living Anionic Copolymerization of Methyl Methacrylate and *tert*-Butyl Acrylate As Promoted by Lithium 2-(2-Methoxyethoxy) Ethoxide

J.-S. Wang, R. Jérôme, Ph. Bayard, M. Patin, and Ph. Teyssié*

Center for Education and Research on Macrmolecules (CERM), University of Liège, Sart-Tilman, B6, 4000 Liège, Belgium

B. Vuillemin and Ph. Heim

Atochem, GRL, BP, 34 Lacq, F-64170 Artix, France

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It has been shown by this laboratory that the formation of complexes between active species and μ-coordinating salts, such as lithium chloride (LiCl), or σ-cation-binding crown ethers, such as dibenzo-18-crown-6 (DB-18-CE-6), was an efficient pathway to prevent secondary transfer and termination reactions[1] and/or to displace a slow equilibrium between different associated propagating species.[2] Using such a ligated technique, homopolymers of methyl methacrylate (MMA) and *tert*-butyl acrylate (tBuA) have been synthesized with a predictable molecular weight and a narrow dispersity,[1] as well as corresponding block copolymers, whichever monomer is first polymerized.[3,4] In sharp contrast, however, a hopefully statistical copolymerization of these two monomers does not proceed as expected and gives very poor results in terms of conversion and molecular weight distribution, as far as LiCl-added initiator is used. This has been accounted for by the occurrence of a selective nucleophilic attack of a highly sensitive methyl ester group by a rather moderately hindered PtBuA anion (i.e., back-biting termination reactions).[5] Nevertheless, a DB-18-CE-6 complexed organosodium initiator [(diphenylmethyl)sodium, Ph_2CHNa] has been shown to avoid such a termination reaction and ensure a perfectly "living" anionic copolymerization of mixtures of MMA and tBuA.[4]

Very recently, it has been discovered by us[6] that a new family of ligands with a unique dual-functional character (i.e., a σ/μ ligand), such as lithium 2-(2-methoxyethoxy) ethoxide (LiOEEM, 1),

$$CH_3OCH_2CH_2OCH_2CH_2OLi$$
1

offers definite advantages versus the former ones, i.e., LiCl and DB-18-CE-6. They allow, even in nonpolar solvents, together with a high activity, the conservation of the living character up to high MW; the direct living polymerization of methacrylates and some acrylates including primary ones; the well-controlled block copolymerization of methacrylates and acrylates whichever monomer is first polymerized; and the control of a high syndiotacticity (i.e., a high T_g) in PMMA (ca. 75–85%).

Now, we report that a LiOEEM-modified initiator is also very efficient in promoting the living statistical copolymerization of mixtures of MMA and tBuA in THF at −78 °C. To keep the same comonomer pair as in the other two ligated systems, i.e., LiCl/Li$^+$ and DB-18-CE-6/Na$^+$, seemed of special interest, since it would allow a direct comparison of different ligands on the living character of related anionic copolymerization processes.

We have previously shown that both MMA and tBuA homopolymerize in a well-controlled manner when exposed to the LiOEEM–Ph_2CHLi initiator system,[6] in THF, at −78 °C, resulting in practically a quantitative yield, high initiator efficiency (over 90%), and very narrow molecular distribution (<1.10). Anionic block copolymerization of MMA and tBuA has also been successful, whichever monomer is first polymerized in the sequential process.[6a] These results suggest that the crossover propagation could in principle take place in the course of statistical copolymerization of MMA and tBuA. As already demonstrated,[5] however, such a hopefully simultaneous copolymerization may be deeply disturbed by a back-biting termination reaction, i.e., a nucleophilic attack of a MMA unit in the antepenultimate position by a terminal PtBuA anion, leading to ill-controlled products.[5]

At this point, the crucial question is thus to know whether a very active ligand, such as LiOEEM, is able to successfully diminish the above-mentioned termination reaction, so as to promote a living "random" copolymerization of mixtures of MMA and tBuA. In order to evaluate this opportunity, (diphenylmethyl)lithium (Ph_2CHLi) complexed with various amounts of LiOEEM has been used to initiate the polymerization of a MMA/tBuA mixture (58/42 mol/mol). Table 1 reports the quite remarkable influence of the LiOEEM/initiator molar ratio on the yield, polydispersity (MWD), and initiation efficiency (*f*) of the final copolymer. In the absence of LiOEEM, the copolymerization is a complicated and ill-controlled process, as evidenced by a very broad multimodal distribution and a low conversion (<20%). However, this situation was considerably improved when only 1 mol of LiOEEM was used per mole of initiator. The conversion of the comonomers significantly increases from 18% up to 80%; at the same time, the MWD of the final copolymer has been reduced from 2.5 to 1.5. However, it should be noted from Table 1 that the initiation efficiency is still low.

The amount of LiOEEM added is obviously a critical parameter. As seen in Table 1, when the molar ratio of LiOEEM per initiator goes from 1 to 5, the initiation efficiency spectacularly increases by a factor greater than 4 (from 0.20 to 0.85), and the MWD of the final copolymer decreases from 1.5 to 1.2. A 10-fold excess of LiOEEM versus the initiator still allows the situation to be further improved. Actually, the conversion of comonomers is quantitative, the initiation efficiency is >90%, and the molecular weight distribution is very narrow, i.e., 1.15. As already seen in the DB-18-CE-6 ligated system,[4] these results imply that crossover propagation proceeds without side termination reactions in the course of these anionic statistical copolymerizations, when the active center is completely complexed by LiOEEM.

When the LiOEEM/initiator molar ratio is still increased over that value of 10, no further beneficial effect is observed. It means that regularly increasing the amount of LiOEEM improves the control of the anionic copolymerization up to an asymptotical situation close to the ideal one but limited at that point as expected for a complex equilibrium formation between the growing ion pairs and the chelating alkoxide 1.

Extension to the other comonomer compositions is straightforward as revealed by the experimental values of yield, initiation efficiency, and MWD (M_w/M_n) of copolymers reported in Table 2. It is obvious indeed that comonomer conversion is almost quantitative in all cases.

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* To whom all correspondence should be addressed.

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Table 1. Effect of LiOEEM/Initiator Molar Ratio on the Anionic Copolymerization of a 58/42 mol/mol Mixture of MMA/tBuA in THF at −78 °C, using Ph_2CHLi as an Initiator[a]

LiOEEM/ initiator[b]	yield (wt %)	$10^{-3}M_n$ (SEC)	M_w/M_n (SEC)	f[c]	mol % tBuA in copolymer	T_g	
						i	m
0	18	23.4	2.50	0.78	92.0	306	311
1	80	77.9	1.50	0.20	54.0	335	343
2	86	42.6	1.30	0.40	45.0	343	350
5	85	18.5	1.20	0.85	44.0	344	350
10	100	21.7	1.15	0.91	42.0	345	351

[a] Initiator concentration: 4×10^{-4} mol/L. [b] mol/mol. [c] Initiator efficiency, $f = M_{n,calc}/M_{n,SEC}$, where $M_{n,calc}$ = (grams of comonomer)/(moles of initiator)(yield/100).

Table 2. Characterization Data of Anionic Copolymerization of Mixtures of MMA and tBuA in THF at −78 °C, Using Ph_2CHLi as an Initiator and LiOEEM as a Ligand

molar fraction in initial feed		yield (wt %)	$10^{-3}M_n$ (SEC)	M_w/M_n (SEC)	f[b]	T_g (K)	
MMA	tBuA					expt	Fox's[c]
100	0	100	20.0	1.10	0.95	401	
92.5	7.5	100	21.0	1.10	0.92	384	391
76.5	23.5	100	20.2	1.15	0.96	363	372
58.0	42.0	100	21.7	1.15	0.91	340	354
37.0	63.0	95	17.4	1.25	0.97	333	337
13.0	87.0	98	19.6	1.25	0.90	325	321
0	100	98	20.0	1.15	0.92	314	

[a] Initiator concentration: 4×10^{-4} mol/L; LiOEEM/Ph_2CHLi = 10/1 (mol/mol). [b] Initiator efficiency, $f = M_{n,calc}/M_{n,SEC}$. [c] $1/T_g = w_{MMA}/T_{g,PMMA} + w_{tBuA}/T_{g,PtBuA}$, where w_{MMA} and w_{tBuA} are the weight fractions of MMA and tBuA units in copolymer, respectively.

The experimental molecular weights as determined by SEC are close to the theoretical values, with an initiation efficiency of 0.93 as an average, and the MWD of the final products is rather narrow, although it slightly increases as the tBuA content in the comonomer feed is increased. Altogether, these are the results expected for a living process, as already observed for the anionic random copolymerization of mixtures of MMA and tBuA as promoted by DB-18-CE-6.[4]

This is in sharp contrast with the significant discrepancies found for the products anionically prepared by using lithium-containing initiator in the absence of LiOEEM (Table 1) and in the presence of LiCl,[5] providing a clear indication that complexation of RLi with LiOEEM is an efficient strategy for avoiding noxious secondary reactions. As reported elsewhere,[7] ^{7}Li and ^{13}C NMR study of a related model system has shown that there exists a unique dual-functional complexation process between a lithium ester enolate and LiOEEM, which convincingly supports the ideas discussed above. Moreover, in comparison with LiCl-complexed active species, the formation of a bulky LiOEEM-complexed σ/μ active complex is most likely at the origin of the anionic living copolymerization of MMA and tBuA.[7]

The samples were further characterized by differential scanning calorimetry (DSC) and carbon-13 NMR spectroscopy. It has been accordingly observed that a PMMA-*b*-PtBuA block copolymer and a mixture of homo-PMMA and -PtBuA both show two T_g's which closely fit the corresponding homopolymers (128 °C for PMMA and 41 °C for PtBuA), indicating an extensive phase separation. In striking contrast, only single T_g's are observed at intermediate positions for all P(MMA-*co*-tBuA) samples (Table 2). As already demonstrated in a preceding paper,[4] these P(MMA-*co*-tBuA) copolymers should thus be reasonably regarded as random ones, rather than block ones or mixtures of two homopolymers.

On the other hand, Figure 1 illustrates the ^{13}C spectra for the block copolymer (Figure 1A), a mixture of PMMA and PtBuA homopolymers (Figure 1B), and P(MMA-*co*-tBuA) copolymer (sample 5 in Table 2) (Figure 1C). In good agreement with DSC measurements, the ^{13}C spectra of the block copolymer and the mixture of homopolymers are almost identical. However, instead of these original resonances, several new peaks (indicated by arrows in Figure 1C) clearly show up in the ^{13}C NMR spectrum of the P(MMA-*co*-tBuA) copolymer, obviously corresponding to different MMA (or tBuA)-centered triad comonomer sequences and related stereochemical configurations of the sequences.[4,8] These results again strongly support the idea that the P(MMA-*co*-tBuA) copolymers anionically prepared by using LiOEEM-complexed initiator are more or less random ones. To gain more direct evidences for the random structure, 1D and 2D NMR characterization of these copolymers is currently being carried out, which will be the subject of a forthcoming paper.

Finally, from an extended Kelen–Tüdös plot,[9] the corresponding monomer reactivity ratios are calculated as $r_{MMA} = 0.29$ and $r_{tBuA} = 6.92$, rather comparable to the values of $r_{MMA} = 0.02$ and $r_{tBuA} = 8.81$ in polymerizations promoted by DB-18-CE-6/Na^+.[4] These data of course confirm that tBuA is more reactive than MMA toward both MMA and tBuA anions in both ligated anionic copolymerization systems.

At this point, it is worth recalling two sets of published results. Müller et al. have already established that, in anionic copolymerization of mixtures of MMA and *tert*-butyl methacrylate (tBuMA) using a Na countercation,[10a] tBuMA is much less reactive than MMA toward both MMA and tBuMA anions, as indicated by $r_{MMA} = 8.2$ and $r_{tBuMA} = 0.17$. In addition, Yuki et al. also reported a similar reactivity order in anionic copolymerization of mixtures of MMA and tBuMA in the presence of Li countercation,[10b] i.e., $r_{MMA} = 35$ and $r_{tBuMA} = 0.43$. Since tBuA is structurally comparable to tBuMA in terms of the ester substituted group, it may thus be concluded that the steric effect of an α-substituted group dominants the relative reactivity of these tBu(M)A in anionic random copolymerization.

In conclusion, a new type of ligand, lithium 2(2-methoxyethoxy) ethoxide (LiOEEM), affords very beneficial effects in the living anionic copolymerization of mixtures of MMA and tBuA, when a lithium-containing initiator is used. Moreover, tBuA units are of great interest, indeed due to their easy hydrolysis into acrylic acid ones; subsequent neutralization of these acidic groups with different bases is accordingly a direct way to produce well-defined PMMA ionomers.

Experimental Section. Reagents and Solvents. MMA and tBA obtained from Norsolor (France) were first vacuum distilled from CaH_2 after reflux and stored under a nitrogen atmosphere at −20 °C. Before polymerization, they were added with a 10 wt % AlEt3 solution in hexane until a persistent yellowish green color was observed. THF was purified by refluxing over a fresh sodium benzophenone complex (a deep purple color indicating an oxygen- and moisture-free solvent).

Initiator. (Diphenylmethyl)lithium (Ph_2CHLi) was prepared at room temperature by reacting diphenylmethane with lithium naphthalene in THF for 24 h. The solution of lithium naphthalene resulted from addition of lithium metal to naphthalene in THF at room temperature.

Preparation of Lithium 2-(2-Methoxyethoxy) Ethoxide (LiOEEM). Under oxygen- and moisture-free argon, equimolar amounts of lithium metal and 2-(2-methoxy-

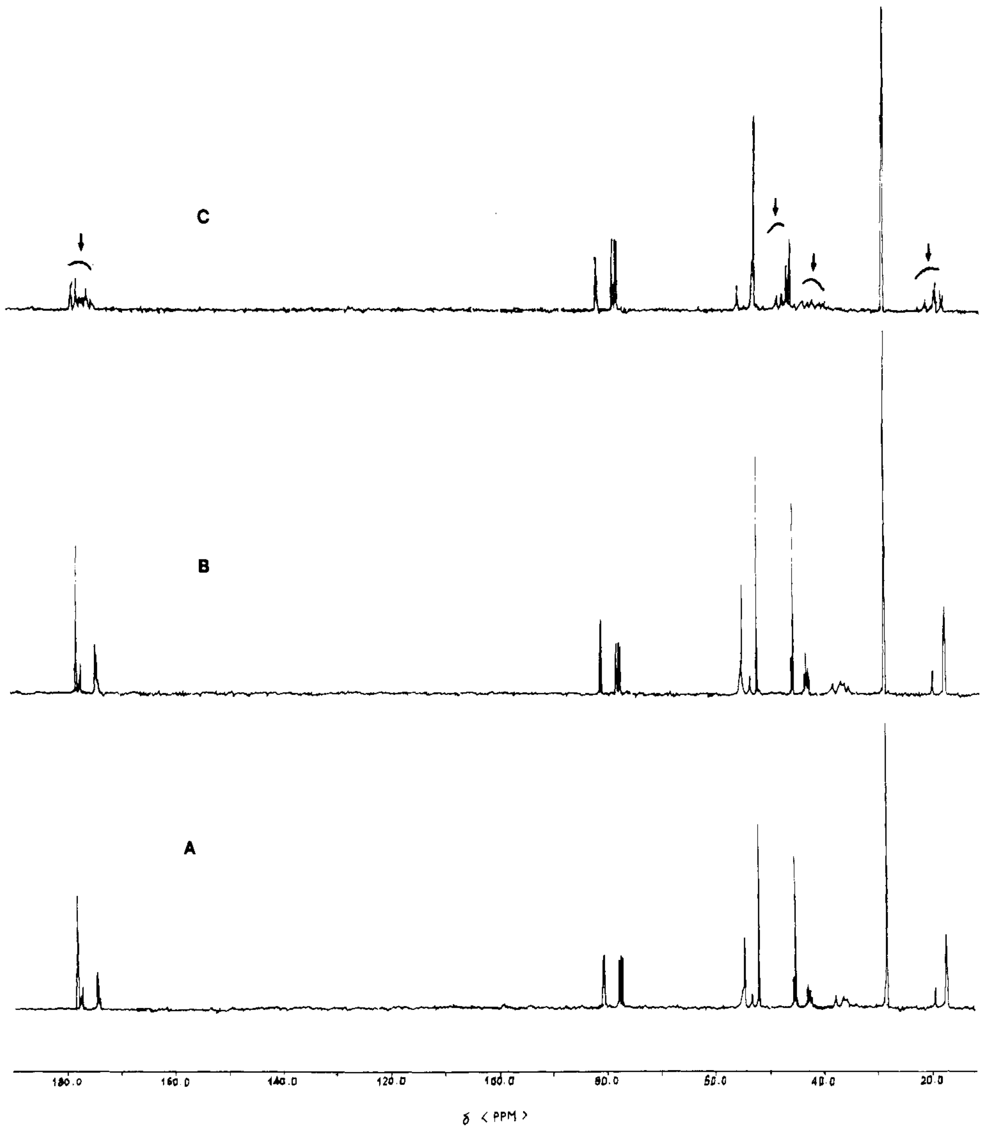

Figure 1. ^{13}C NMR spectra of different types of PMMA- and PtBuA-based polymers. (A) PMMA-*b*-PtBuA diblock copolymer (M_n = 21 000–20 000), (B) 50/50 (w/w) mixture of homo-PMMA (M_n = 20 000) and homo-PtBuA (M_n = 20 000), (C) P(MMA-*co*-tBuA) copolymer (sample 5, Table 2).

ethoxy)ethanol were added into THF in a dry flask equipped with an inert gas inlet, a magnetic stir bar, and a water-cooled condensor. The solution was heated to reflux and the reaction allowed to continue overnight.

Copolymerization. Anionic copolymerization of mixtures of MMA and tBuA was carried out in a flamed glass reactor under a nitrogen atmosphere. THF, ligand, and initiator were transferred into the glass reactor by using a rubber septum and a stainless steel capillary or a syringe. The initiator solution was added dropwise to THF containing LiOEEM ligand until the initiator color persisted; ca. 5 drops of a 0.2 M initiator solution to 100 mL of a THF/LiOEEM solution was generally required to get a persistent color, i.e., a highly pure solvent and ligand. After adding the desired amount of initiator, the solution was cooled to −78 °C, the required quantity of MMA and tBuA was introduced, and the copolymerization was performed from a few seconds to 1 h depending on the monomer conversion requirements. It was then stopped by adding acidic methanol, and the copolymer, recovered by precipitation into methanol or into a methanol/water (50/50) mixture. The crude polymer was dried under vacuum at 80 °C for 48 h.

Characterization. SEC was carried out by using a Hewlett-Packard 1090 liquid chromatograph equipped with four columns (10^5, 10^3, 500 and 100 Å) and a Hewlett-Packard 1037A refractive index detector. Polystyrene standards were used for calibration, and the number- (M_n) and weight-average (M_w) molecular weights as well as polydispersity of the polymer were accordingly calculated. The glass transition temperature was measured by differential scanning calorimetry (DSC) using a DuPont 9000 apparatus. The instrument was calibrated with indium and mercury. Samples were first heated up to 150 °C, cooled rapidly to room temperature, and then scanned again at a rate of 20 °C min^{-1}. Compositional and structural analyses of the copolymers were performed by means of ^{1}H and inverse-gated proton-decoupling ^{13}C NMR using a Bruker AM 400 spectrometer. Monomer reactivity ratios were determined according to the extended Kelen–Tüdös (EKT) method.[9]

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